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(54) Title: PROCESS FOR MAKING A DETERGENT COMPOSITION

(57) Abstract: A process for making a granular detergent composition including the steps of: (a) granulating a detersive material that includes a detergent surfactant and a builder; (b) spraying a buffering agent on the granules to substantially coat the granules; (c) drying the granules with a gas that has from about 0.05 % to 5.0 % by weight of carbon dioxide. The buffering agent should have a buffering capability that maintains the pH on the surface of the granule to less than about 13.5.

PROCESS FOR MAKING A DETERGENT COMPOSITION

FIELD

The present invention relates to a process for making a detergent. Specifically, the present invention relates to a process for making a detergent composition having improved physical properties.

BACKGROUND

There is a current trend for commercially available granular detergent compositions that have higher bulk densities as well as higher active ingredient content. Such granular detergent compositions offer greater convenience to the consumer and they reduce the amount of packaging materials that will ultimately be disposed of.

The traditional method for making granular detergents is spray drying. Typically, detergent ingredients such as surfactants, builders, silicates and carbonates are mixed in a tank to form a slurry which is about 35% to about 50% water. This slurry is then atomized in a spray drying tower to reduce moisture to below about 10%. Finally, brighteners, perfumes, enzymes and other detergent adjuvants are added to or sprayed onto the granules.

In the granules, there are some sources of alkalinity in the final product formulations, for example, sodium aluminosilicates builder, sodium carbonates, and in practice the final products will tend to contain localized regions of excess caustic or very high alkalinity. This can cause localized discoloration of the product, particularly yellowing, where alkali-sensitive ingredients such as

perfumes and brighteners are present. This manifests itself as the yellowing of some particles within the powder, the number of yellow particles and the intensity of their color tends to increase with time.

Various approaches for preventing discoloration of detergent compositions have been tried by detergent manufacturers. One approach is to decrease the amount of sodium hydroxide which neutralizes any acidic component in the matrix. Another approach is to add a carboxylic acid, such as monosodium glutamate, in the process. However, these approaches are not sufficient to fully prevent discoloration.

Based on the foregoing, there is a need for a process which provides a granular detergent composition having improved physical properties including the prevention of discoloration.

SUMMARY

The present invention is directed to a process for making a granular detergent composition comprising the steps of (a) granulating a detersive material comprising a detergent surfactant and a builder, (b) spraying a buffering agent on the granules to substantially coat the granules, (c) drying the granules with a gas comprising from about 0.2% to 10% by weight of carbon dioxide. The buffering agent in the present invention has a buffering capability that maintains the pH on the surface of the granule to less than about 13.5.

The process of the present invention can prevent granules from turning yellow and provide granules with improved white color. Further, the process of the present invention can provide granules with improved odor.

These and other features, aspects, and advantages of the present invention will become better understood from a reading of the following description, and appended claims.

DETAILED DESCRIPTION

While the specification concludes with claims particularly pointing out and distinctly claiming the invention, it is believed that the present invention will be better understood from the following description.

All percentages, ratios, and levels of ingredients referred to herein are based on the actually total amount of the composition, unless otherwise indicated.

All measurements referred to herein are made at 25°C unless otherwise specified.

All publications, patent applications, and issued patents mentioned herein are hereby incorporated in their entirety by reference. Citation of any reference is not an admission regarding any determination as to its availability as prior art to the claimed invention.

Definitions

Herein, "comprising" means that other steps and other ingredients which do not affect the end result can be added. This term encompasses the terms "consisting of" and "consisting essentially of."

Herein, "mixtures" is meant to include a simple combination of materials and any compounds that may result from their combination.

Herein, "cold water" means water which has a temperature of below 30°C.

Herein, "density" means bulk density unless specifically stated otherwise.

All ingredients such as detersive surfactants and builders useful herein may be categorized or described by their benefit or their postulated mode of action. However, it is to be understood that the ingredients useful herein can, in some instances, provide more than one benefit or operate via more than one mode of action. Therefore, classifications herein are made for the sake of convenience and are not intended to limit an ingredient to the particularly stated application or applications listed.

The Detergent Making Process

The present invention is directed to a process for making a granular detergent composition comprising the steps of (a) granulating a detersive material comprising a detergent surfactant and a builder, (b) spraying a buffering agent on the granules to substantially coat the granules, (c) drying the granules with a gas comprising from about 0.2% to 10% by weight of carbon dioxide. The buffering agent in the present invention has a buffering capability that maintains the pH on the surface of the granule to less than about 13.5.

Also the present invention is directed to a granular detergent composition which is made according to the process described here.

Further, the present invention is directed to the granular detergent composition having a delta E difference of less than 2.0, preferably, less than 1.0 having an Odor evaluation of at least 7.0, preferably, 8.0

Furthermore, the present invention is directed to the granular detergent composition being packed in the package having less than 50g/m2/24 hours, preferably, 30g/m2/24 hours, more preferably, 15g/m2/24 hours of moisture vapour transmission rate (MVTR).

The process of the present invention can prevent granules from turning yellow and provide granules with improved white color.Further, the process of the present invention can provide granules with improved odor. Not wanting to be limited by theory, there are some sources of high alkalinity in the final product formulations, for example, sodium aluminosilicate builder, sodium silicate, sodium carbonate or sodium excess hydroxide or caustic in anionic surfactant paste (AS etc.). This can cause localized discoloration of the product, particularly yellowing, where alkali-sensitive ingredients such as perfumes are present. Perfumes usually contain primary alcohol and aldehyde groups in the molecules. In the high alkaline condition, the primary alcohol groups are easily converted to aldehydes and these resulting aldehydes and the originally present aldehyde groups are easily condensed by aldol reaction and the resulting hyperconjugation in the resulting molecules tend to have a yellow color. Further, because the primary alcohol and aldehyde groups in the perfume molecules react with the alkaline sources in the granules, the odor of the perfume is changed. As a result, the odor of the final product may not be acceptable for consumers.

In step (b) of the present invention, spraying a buffering agent on the granules to substantially coating them, reduces the alkalinity of the granular surface. Also, in step (c), drying the granules with a gas comprising from about 0.05% to about 10% by weight of carbon dioxide, regulates the pH on the surface of the granules to be from about 8.0 to about 12.5 of pH. Therefore, the primary alcohol and aldehyde groups in perfumes and alkaline sources in the granules tend to react less. As a result, the present invention can provide granular detergent products with improved color and odor.

The process steps are described in greater detail below.

A. Granulating step

The first step for preparing the granular detergent compositions of the present invention is granulating a detersive material comprising a detergent surfactant and a builder. Any process and equipment that is conventionally used for preparing granules can be used in the processes defined herein. Preferably, the detersive material is applied in the form of an aqueous slurry. Herein, "slurry" refers to a mixture of a detergent surfactant and a builder, which is not substantially solid in form. The slurry can also include other ingredients such as brighteners and buffers.

Spray-drying of the slurry mixtures is preferable, especially for aqueous slurry mixtures to form spray-dried granules., . More preferably, spray-drying in relatively tall spray drying towers is useful. The spray drying processes useful herein include dispersing an aqueous slurry or mixture under high pressure through nozzles down a spray drying tower through which hot gases are counter-currently flowing, that is, the hot gasses flow up through the tower. This step can be carried out in conventional spray drying equipment such as the aforementioned towers as well as other spray drying apparatus. The spray-dried granules, that are subsequently used as part of the overall process, can be compacted by a compacting machine. The aqueous slurry used comprises the anionic surfactant, the builder, and no more than about 1.0%, preferably about 0%, by weight of nonionic surfactant. The amount of nonionic surfactant in the aqueous slurry is based on limitations concerning environmental and safety concerns (plume opacity, auto-oxidation) and limitations concerning the physical properties of the slurry used during the spray drying process. Nonionic surfactant can be used in the composition of the present invention, but it should be added after the spray drying process.

After spray-drying, the granules from a tower can be densified further by loading a liquid such as water or a nonionic surfactant into the pores of the granules and/or subjecting them to one or more high speed mixer/densifiers. A suitable high speed mixer/densifier for this process is a device marketed under the tradename "Lödige CB 30" or "Lödige CB 30 Recycler" which comprises a static cylindrical mixing drum having a central rotating shaft with mixing/cutting blades mounted thereon. In use, the ingredients for the composition are introduced into the drum and the shaft/blade assembly is rotated at speeds in the range of 100-2500 rpm to provide thorough mixing/densification. See U.S.

Patent 5,149,455, Jacobs et al, issued September 22, 1992, and U.S. Patent 5,565,422, Del Greco et al, issued October 15, 1996. Other such apparatus includes the devices marketed under the tradename "Shugi Granulator" and under the tradename "Drais K-TTP 80".

Another process step which can be used to further densify spray-dried granules involves treating the spray-dried granules in a moderate speed mixer/densifier. Equipment such as that marketed under the tradename "Lödige KM" (Series 300 or 600) or "Lödige Ploughshare" mixer/densifiers are suitable for this process step. Such equipment is typically operated at 40-160 rpm. The residence time of the detergent ingredients in the moderate speed mixer/densifier is from about 0.1 to 12 minutes conveniently measured by dividing the steady state mixer/densifier weight by the throughput (*e.g.*, Kg/hr). Other useful equipment includes the device which is available under the tradename "Drais K-T 160." This process step which employs a moderate speed mixer/densifier (*e.g.*, Lödige KM) can be used by itself or sequentially with the aforementioned high speed mixer/densifier (*e.g.*, Lödige CB) to achieve the desired density. Other types of granules manufacturing apparatus useful herein include the apparatus disclosed in U.S. Patent 2,306,898, G. L. Heller, issued December 29, 1942.

While it may be more suitable to use the high speed mixer/densifier followed by the low speed mixer/densifier, the reverse sequential mixer/densifier configuration also can be used. One or a combination of various parameters including residence times in the mixer/densifiers, operating temperatures of the equipment, temperature and/or composition of the granules, the use of adjunct ingredients such as liquid binders and flow aids, can be used to optimize densification of the spray-dried granules in the process of the invention. By way of example, see the processes in U.S. Patent 5,133,924, Appel et al, issued July 28, 1992; U.S. Patent 4,637,891, Delwel et al, issued January 20, 1987; U.S. Patent 4,726,908, Kruse et al, issued February 23, 1988; and, U.S. Patent 5,160,657, Bortolotti et al, issued November 3, 1992.

In those situations in which particularly heat sensitive or highly volatile detergent ingredients are to be incorporated into the final detergent composition, processes which do not include spray drying towers are preferred. The formulator can eliminate the spray-drying step by feeding, in either a continuous or batch mode, starting detergent ingredients directly into mixing equipment that is commercially available. One particularly preferred embodiment involves

charging a surfactant paste and an anhydrous material into a high speed mixer/densifier (*e.g.*, Lödige CB) followed by a moderate speed mixer/densifier (*e.g.*, Lödige KM) to form high density detergent agglomerates. See U.S. Patent 5,366,652, Capeci et al, issued November 22, 1994 and U.S. Patent 5,486,303, Capeci et al, issued January 23, 1996. Optionally, the liquid/solids ratio of the starting detergent ingredients in such a process can be selected to obtain high density agglomerates that are more free flowing and crisp. See U.S. Patent 5,565,137, Capeci et al, issued October 15, 1996.

Optionally, the process may include one or more recycle streams of undersized particles produced by the process which are fed back to the mixer/densifiers for further agglomeration or build-up. The oversized particles produced by this process can be sent to grinding apparatus and then fed back to the mixing/densifying equipment. These additional recycle process steps facilitate build-up agglomeration of the starting detergent ingredients resulting in a finished composition having a uniform distribution of the desired particle size and density (> 300 g/l). See U.S. Patent 5,516,448, Capeci et al, issued May 14, 1996 and U.S. Patent 5,489,392, Capeci et al, issued February 6, 1996. Other suitable processes which do not call for the use of spray-drying towers are described by U.S. Patent 4,828,721, Bollier et al, issued May 9, 1989; U.S. Patent 5,108,646, Beerse et al, issued April 28, 1992; and, U.S. Patent 5,178,798, Jolicoeur, issued January 12, 1993.

In yet another embodiment, a high density detergent composition using a fluidized bed mixer. In this process, the various ingredients of the finished composition are combined in an aqueous slurry (typically 80% solids content) and sprayed into a fluidized bed to provide the finished detergent granules. Prior to the fluidized bed, this process can optionally include the step of mixing the slurry using the aforementioned Lödige CB mixer/densifier or a "Flexomix 160" mixer/densifier, available from Shugi. Fluidized bed or moving beds of the type available under the tradename "Escher Wyss" can be used in such processes.

Another suitable process which can be used herein involves feeding a liquid acid precursor of an anionic surfactant, an alkaline inorganic material (*e.g.*, sodium carbonate) and optionally other detergent ingredients into a high speed mixer/densifier so as to form particles containing a partially or totally neutralized anionic surfactant salt and the other starting detergent ingredients. Optionally, the contents in the high speed mixer/densifier can be sent to a moderate speed

mixer/densifier (*e.g.*, Lödige KM) for further mixing resulting in the finished high density detergent composition. See U.S. Patent 5,164,108, Appel et al, issued November 17, 1992.

Optionally, high density detergent compositions according to the invention can be produced by blending conventional or densified spray-dried detergent granules with detergent agglomerates in various proportions (*e.g.*, a 60:40 weight ratio of granules to agglomerates) produced by one or a combination of the processes discussed herein. See U.S. Patent 5,569,645, Dinniwell et al, issued October 29, 1996. Additional adjunct ingredients such as enzymes, perfumes, brighteners and the like can be sprayed or admixed with the agglomerates, granules or mixtures thereof produced by the processes discussed herein.

(1) Detergent Surfactant

The granular detergent compositions produced by the process of the present invention comprise from about 5% to about 80%, more preferably from about 10% to about 70%, most preferably from about 15% to about 40%, by weight of the composition, of detergent surfactant.

The detergent surfactant can be selected from the group consisting of anionic surfactants, nonionic surfactants, zwitterionic surfactants, ampholytic surfactants, cationic surfactants, and mixtures thereof; more preferably anionic surfactants, nonionic surfactants and mixtures thereof.

More specifically, the granular detergent compositions of the present invention comprise from about 5% to about 80% of anionic surfactant, preferably from about 10% to about 70%, most preferably 15% to about 40% by weight.

Water-soluble salts of the higher fatty acids, *i.e.*, soaps, are useful anionic surfactants in the compositions herein. Such salts include alkali metal soaps such as the sodium, potassium, ammonium, and alkylolammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms, and preferably from about 12 to about 18 carbon atoms. Soaps can be made by direct saponification of fats and oils or by the neutralization of free fatty acids. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, *i.e.*, sodium or potassium tallow and coconut soap.

Useful anionic surfactants also include the water-soluble salts, preferably the alkali metal, ammonium and alkylolammonium salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing

from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups.) Examples of this group of synthetic surfactants are the sodium and potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C_{12-18} carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil; and the sodium and potassium alkylbenzene sulfonates in which the alkyl group contains from about 10 to about 16 carbon atoms, in straight chain or branched chain configuration. See U.S. Patent No. 2,220,099 and 2,477,383. Especially valuable are linear straight chain alkylbenzene sulfonates in which the average number of carbon atoms in the alkyl group is from about 11 to 14, abbreviated as C_{11-14} LAS.

Especially preferred are mixtures of C_{11-16} (preferably C_{11-13}) linear alkylbenzene sulfonates and C_{12-18} (preferably C_{14-16}) alkyl sulfates. These are preferably present in a weight ratio of between 4:1 and 1:4, preferably about 3:1 to 1:3, alkylbenzene sulfonate: alkyl sulfate. Sodium salts of the above are preferred.

Other anionic surfactants useful herein are the sodium alkyl glyceryl ether sulfonates and water-soluble salts of esters of alpha-sulfonated fatty acids. Examples of these anionic surfactants are set forth in U.S. Patent 5,565,422, Del Greco, issued October 15, 1996.

The granular detergent compositions of the present invention useful herein may also comprise nonionic surfactant. As discussed above, the nonionic surfactant should be added after the spray drying process. But depending on the nonionic surfactant, small amount of the nonionic surfactant can be incorporated into the composition as an integral part of the spray dried granule and/or via the spraying step of the process herein. Preferably, almost all of the nonionic surfactant is incorporated after mixing and/or grinding the granules.

Water-soluble nonionic surfactants are used in the instant detergent compositions. Such nonionic materials include compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. The length of the polyoxyalkylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Suitable nonionic surfactants include the polyethylene oxide condensates of alkyl phenols, *e.g.*, the condensation products of alkyl phenols having an alkyl group containing from about 6 to 15 carbon atoms, in either a straight chain or branched chain configuration, with from about 3 to 80 moles of ethylene oxide per mole of alkyl phenol.

Included are the water-soluble and water-dispersible condensation products of aliphatic alcohols containing from 8 to 22 carbon atoms, in either straight chain or branched configuration, with from 3 to 12 moles of ethylene oxide per mole of alcohol.

Semi-polar nonionic surfactants include water-soluble amine oxides containing one alkyl moiety of from abut 10 to 18 carbon atoms and two moieties selected from the group of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of about 10 to 18 carbon atoms and two moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to 3 carbon atoms.

Preferred nonionic surfactants are of the formula $R^1(OC_2H_4)OH$, wherein R^1 is a C_{10-16} alkyl group or a C_{8-12} alkyl phenyl group, and n is from 3 to about 80.

Particularly preferred are condensation products of alcohols with from about 5 to about 20 moles of ethylene oxide per mole of alcohol, *e.g.*, C_{12-13} alcohol condensed with about 6.5 moles of ethylene oxide per mole of alcohol.

In a preferred embodiment, the nonionic surfactant is an ethoxylated surfactant derived from the reaction of a monohydroxy alcohol or alkylphenol containing from about 8 to about 20 carbon atoms, excluding cyclic carbon atoms, with from about 6 to about 15 moles of ethylene oxide per mole of alcohol or alkyl phenol on an average basis.

A particularly preferred ethoxylated nonionic surfactant is derived from a straight chain fatty alcohol containing from about 16 to about 20 carbon atoms (C_{16-20} alcohol), preferably a C_{18} alcohol, condensed with an average of from about 6 to about 15 moles, preferably from about 7 to about 12 moles, and most preferably from about 7 to about 9 moles of ethylene oxide per mole of alcohol.

Preferably the ethoxylated nonionic surfactant so derived has a narrow ethoxylate distribution relative to the average.

The ethoxylated nonionic surfactant can optionally contain propylene oxide in an amount up to about 15% by weight of the surfactant and retain the advantages hereinafter described. Preferred surfactants of the invention can be prepared by the processes described in US Patent 4,223,163, Builloty, issued September 16, 1980.

A highly preferred composition contains the ethoxylated monohydroxyalcohol or alkyl phenol and additionally comprises a polyoxyethylene, polyoxypropylene block polymeric compound; the ethoxylated monohydroxy alcohol or alkyl phenol nonionic surfactant comprising from about 20% to about 80%, preferably from about 30% to about 70%, of the total surfactant composition by weight.

Suitable block polyoxyethylene-polyoxypropylene polymeric compounds that meet the requirements described hereinbefore include those based on ethylene glycol, propylene glycol, glycerol, trimethylolpropane and ethylenediamine as the initiator reactive hydrogen compound. Polymeric compounds made from a sequential ethoxylation and propoxylation of initiator compounds with a single reactive hydrogen atom, such as C_{12-18} aliphatic alcohols, do not provide satisfactory suds control in the detergent compositions of the invention. Certain of the block polymer surfactant compounds designated PLURONIC and TETRONIC by the BASF-Wyandotte Corp., Wyandotte, Mich., are suitable in the surfactant compositions of the invention.

A particularly preferred embodiment contains from about 40% to about 70% of a polyoxypropylene, polyoxyethylene block polymer blend comprising about 75%, by weight of the blend, of a reverse block co-polymer of polyoxyethylene and polyoxypropylene containing 17 moles of ethylene oxide and 44 moles of propylene oxide; and about 25%, by weight of the blend, of a block co-polymer of polyoxyethylene and polyoxypropylene, initiated with trimethylol propane, containing 99 moles of propylene oxide and 24 moles of ethylene oxide per mole of trimethylol propane.

Because of the relatively high polyoxypropylene content, *e.g.*, up to about 90% of the block polyoxyethylene-polyoxypropylene polymeric compounds of the invention and particularly when the polyoxypropylene chains are in the terminal position, the compounds are suitable for use in the surfactant compositions of the

invention and have relatively low cloud points. Cloud points of 1% solutions in water are typically below about 32 degC and preferably from about 15 degC to about 30 degC for optimum control of sudsing throughout a full range of water temperatures and water hardnesses.

In addition, the anionic and nonionic surfactants required in the detergent compositions of the invention herein, the detergent compositions may also contain surfactants selected from the group of ampholytic, zwitterinoic, cationic surfactants and mixtures thereof.

Ampholytic surfactants include derivatives of aliphatic or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic moiety can be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and at least one aliphatic substituent contains an anionic water-solubilizing group.

Zwitterionic surfactants include derivatives of aliphatic, quaternary, ammonium, phosphonium, and sulfonium compounds in which one of the aliphatic substituents contains from about 8 to 18 carbon atoms.

Cationic surfactants can also be included in the present detergent granules. Cationic surfactants comprise a wide variety of compounds characterized by one or more organic hydrophobic groups in the cation and generally by a quaternary nitrogen associated with an acid radical.

Pentavalent nitrogen ring compounds are also considered quaternary nitrogen compounds. Halides, methyl sulfate and hydroxide are suitable.

Tertiary amines can have characteristics similar to cationic surfactants at washing solution pH values less than about 8.5. A more complete disclosure of these and other cationic surfactants useful herein can be found in US Patent 4,228,044, Cambre, issued Oct. 14, 1980.

Cationic surfactants are often used in detergent compositions to provide fabric softening and/or antistatic benefits. Antistatic agents which provide some softening benefit and which are preferred herein are the quaternary ammonium salts described in US Patent 3,936,537, Baskerville, Jr. et al., issued February 3, 1976. Useful cationic surfactants also include those described in US Patent 4,222,905, Cockrell, issued September 16, 1980, and in US Patent 4,239,659, Murphy, issued December 16, 1980.

(2) Builders

Builders are typically employed to sequester hardness ions and to help adjust the pH of the laundering liquid. Such builders are present in the compositions up to about 85%, preferably from about 5% to about 50%, most preferably from about 10% to about 30% to provide their builder and pH-controlling functions. The builders herein include any of the conventional inorganic and organic water-soluble builder salts.

Such builders include water-soluble salts of phosphates, *e.g.*, such as tripolyphosphates, pyrophosphates, orthophosphates, higher polyphosphates, other carbonates, silicates, and organic polycarboxylates. Specific preferred examples of inorganic phosphate builders include sodium and potassium tripolyphosphates and pyrophosphates.

Nonphosphorus-containing material may also be selected. Specific examples of nonphosphorus, inorganic detergent builder ingredients include water-soluble bicarbonate, carbonate, and silicate salts. The alkali metal, e.g., sodium and potassium, bicarbonates, carbonate and silicates are particularly useful herein.

Aluminosilicate ion exchange materials useful in the practice of this invention are commercially available. The aluminosilicates useful in this invention can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is discussed in Krummel et al, US Patent 3,985,669, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite B, and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material in Zeolite A and has the formula $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]xH_2O$ wherein x is from about 20 to about 30, especially about 27. Other preferred builder include a mixture of a water-insoluble aluminosilicate builder such as zeolite A or of a layered silicate (*e.g.*, SKS-6), and a water-soluble carboxylate chelating agent such as citric acid. Still other preferred builder include a mixture of a water-insoluble aluminosilicate builder such as zeolite A, and a watersoluble carboxylate chelating agent such as citric acid. Preferred builder systems for use in liquid detergent compositions of the present invention are soaps and polycarboxylates.

Water-soluble, organic builders are also useful herein. For example, the alkali metal, polycarboxylates are useful in the present compositions. Specific examples of the polycarboxylate builder salts include sodium and potassium, salts of ethylenediaminetetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acid, polyacrylic acid, and polymaleic acid. Other desirable polycarboxylate builders are the builders set forth in Diehl, US Patent 3,308,067, Examples of such materials include the water-soluble salts of homo- and co-polymers of aliphatic carboxylic acids such as maleic acid, itaconic acid, mesaconic acid, fumaric acid, aconitic acid, citraconic acid, and methylenemalonic acid.

Other suitable polymeric polycarboxylates are the polyacetal carboxylates described in Crutchfield et al, U.S. Patent 4,144,226, issued March 13, 1979, and U.S. Patent 4,246,495, issued March 27, 1979. These polyacetal carboxylates can be prepared by bringing together under polymerization conditions an ester of glyoxylic acid and a polymerization initiator. The resulting polyacetal carboxylate ester is then attached to chemically stable end groups to stabilize the polyacetal carboxylate against rapid depolymerization in alkaline solution, converted to the corresponding salt, and added to a surfactant.

The compositions herein preferably contain little (*e.g.*, less than 10%, preferably less than 5%, by weight) or no phosphate builder materials. The presence of higher levels of tripolyphosphate improves solubility of the compositions to the point where hydrophobic amorphous silicate provides little or no additional improvements. However, sodium pyrophosphate reduces solubility so that the benefit provided by the hydrophobic amorphous silicate is greater in granular compositions containing pyrophosphate.

B. Buffer Spraying

The second step for making a granular detergent composition of the present invention is spraying a buffering agent onto the granules to substantially coat the granule obtained by the first step of the process.

Without being bound by theory, it is believed that surfactants, particularly nonionic surfactants, contained in detersive materials, tend to change to gel-like formation when exposed to humidity or when contacted with water in the washing solution. If the nonionic surfactant becomes gel-like, it may seep out of the granule particles during processing of detergent compositions. This seepage

may harden on the exterior of the granule covering the detersive material, which, in turn, may inhibit the dissolution of the detersive material.Also, the gel-like formation can make the particles stick together to form large agglomerates. Such large agglomeration may also slow or inhibit the dissolution of detergent particles.

It is believed that the buffering agent used in the present invention is not gel-like when exposed to humidity. As such, the resulting granules are not sticky and have good dissolution/dispersion properties.

Preferably, the buffering agent is applied by spraying it onto the surface of the granules prepared by the granulating step. The concentration of the buffering agents are from about 0.5% to about 95%, preferably from 1.0% to about 50% by weight of the spray composition.

Preferably, the buffering agent is selected from the group consisting of sodium and potassium salts of carbonate, bicarbonate, sulfate, hydrogen sulfate, phosphate, monohydrogen phosphate, dihydrogen phosphate, citrate, monohydrogen citrate, dihydrogen citrate, acetate, silicate, pyrophosphate, monohydrogen pyrophosphate, dihydrogen pyrophosphate, trihydrogen pyrophosphate, tripolyphosphate, monohydrogen tripolyphosphate, dihydrogen tripolyphosphate, trihydrogen tripolyphosphate and mixtures thereof. Some of the preferred buffering agents are also useful as builders described above.

Buffering agents useful herein are applied in an amount of from about 0.5% to about 50% by the total weight of detergent components, preferably from about 0.5% to about 25%, more preferably, from about 0.5% to about 10%. The temperature of the buffering agent during coating step is from about 10°C to about 100°C, preferably from about 30°C to about 70°C.

The buffering agent should have a buffering capability that maintains the pH to less than about 13.5, preferably, from about 8.0 to about 12.0 on the surface of the granule. The surface of the granules from step (a) may be considered high alkalinity. One of the roles of the buffering agent is to reduce the pH on the surface of the granules to less than 13.5, preferably, from about 8.0 to about 12.0. If the pH of the buffering agent is 13.5 above, no effects are expected in terms of improving product color and odor, if the pH of the buffering is below 8.0, it may affect product performance since detergents are designed to work well at alkaline conditions during washing.

The process for preparing a granular detergent composition may further comprise the step of applying a shell to the surface of the buffering agent coated detergent granules. Herein, "shell" means a material which covers the granules of detersive material to prevent agglomeration of the particles. The detergent granules covered by shell can provide increased bulk density and reduced friction between particles; thus, the volume of the product can be reduced, providing a more compact product to the consumer. Preferably, the concentration of the shell is from about 1% to about 50%, preferably from about 2% to about 30%, more preferably, from about 2% to 15%. The shell useful herein is selected from the group consisting of fine inorganic materials having a mean particle size less than about 5 μm, a micronized crystalline layered silicate (SKS-6 avairable from Hoechst Inc.,), a micronized carbonate, a micronized sodium sulphate, aluminosilicate (Zeolite), magnesium silicate, calcium silicate, and clay, preferably Zeolite.

It is believed that the adding the shell into the buffering agent or over the coating of inorganic solution tends to provide improved flowability. Preferably, the ratio of the buffering agent to the shell is from about 0.2 to about 7.0.

C. Drying step

The third step for making a granular detergent composition of the present invention is drying the granules obtained by step (b) with a gas. The gas comprises from about 0.05% to about 10%, preferably, from about 0.2% to about 5%, more preferably, from about 0.3% to about 4% by weight of carbon dioxide.

The role of the carbon dioxide is to reduce the pH of the surface of the granules obtained from step (b).

Odor evaluation system

The odor of the granule detergent composition of the present invention was measured by the following.

A sample of detergent granules made according to the processes herein are placed in an odorless plastic cup. The granules should fill the cup 1cm from the bottom of the cup, then it is graded against an odor standard sample by at least three qualified odor graders in an odor panel room. Then, the grade results are averaged.

A And also the product is applied for perfume stability test (Rapid Aging Test, RAT). That product is packed in common package, for example, polyethylene package and stored at 49.5 °C room for 10 days. This is an accelerated condition to predict the odor quality of a product stored for six months under normal conditions The product was then evaluated for its odor, as described above. Accordingly, the granule detergent composition of the present invention showed better odor evaluation value even after the RAT.

Color evaluation system

The color of the granule detergent composition of the present invention was measured by Hunter color evaluation. The color data consists of three values: "L" (0: black to 100: white), "a" (minus a: green, plus a: red) and "b" (minus b: blue, plus b: yellow).

These values are measured before RAT and after RAT by Top scan, TC-1800 DO" supplied by Tokyo denshoku and Delta E is calculated by the following equation.

$$\text{Delta E} = \text{Route}((L-L0)2+(a-a0)2+(b-b0)2)$$

wherein L0, a0 and b0 are the color data values before RAT, L, a, b are the color data values after RAT.

The granular detergent composition of the present invention has a Delta E of less than 2 while numerous granular detergent compositions made according to conventional processes have a Delta E of more than 2.

Packaging system

The granular detergent composition of the present invention is preferably packed within a packaging system having a moisture vapour transmission rate of less than 50g/m3/24 hours. The moisture vapour transmission rate is preferably less than 30g/m3/24 hours, more preferably, 20g/m3/24 hours.

If the detergent composition of the present invention is packed without the packaging system, the detergent composition may not retain odor. The odor of the detergent can be retained longer by packing in the packaging system because perfume is a volatile material.

Materials for the closed packaging system are not limited. Preferably, the material is selected from the group consisting of polyethylene, polypropylene, polyethylene terephthalate (PET), laminate coated paper and mixtures thereof.

Other Ingredients

Bleaching agents and activators additionally useful herein are described in U.S. Patent 4,412,934, Chung et al., issued November 1, 1983; U.S. Patent 4,483,781, Hartman, issued November 20, 1984; U.S. Patent 4,634,551, Burns et al, issued January 6, 1987; and U.S. Patent 4,909,953, Sadlowski et al, issued March 20, 1990. Chelating agents are described in U.S. Patent 4,663,071, Bush et al. Suds modifiers are also optional ingredients and are described in U.S. Patent 3,933,672, Bartoletta et al., issued January 20, 1976; and U.S. Patent 4,136,045, Gault et al., issued January 23, 1979. Suitable smectite clays for use herein are described in U.S. Patent 4,762,645, Tucker et al, issued August 9, 1988. Suitable additional detergency builders for use herein are enumerated in U.S. Patent 3,936,537, Baskerville, Jr. et al., issued February 3, 1976, and in U.S. Patent 4,663,071, Bush et al, issued May 5, 1987.

Other ingredients suitable for inclusion in a granular detergent composition can be added to the present compositions. These include bleach activators, suds boosters or suds suppressors, anti-tarnish and anticorrosion agents, soil suspending agents, soil release agents, germicides, pH adjusting agents, non-builder alkalinity sources, enzymes, enzyme-stabilizing agents and perfumes. Such ingredients are described in the Baskerville, Jr's U.S. Patent referred to the above.

EXAMPLES

The following examples further describe and demonstrate embodiments within the scope of the present invention. The examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention, as many variations thereof are possible without departing from the spirit and scope of the invention. Where applicable, ingredients are identified by chemical or CTFA name, or otherwise defined below.

In the detergent compositions, unless otherwise specified, the detergent ingredients are expressed by weight of the total compositions. The abbreviated component identifications therein have the following meanings:

C12LAS	Sodium linear C_{11-13} alkyl benzene sulphonate
C12-18FAS	C12-C18 Fatty alcohol sulfate
STPP	Sodium tripolyphosphate
Brighteners/FWA 49	Disodium 4,4'-bis(2-sulphostyryl)biphenyl.
Brighteners/FWA 3	Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl) stilbene-2:2'-disulfonate.
Sodium Silicate (45% active)	Amorphous Sodium Silicate (SiO_2:Na_2O ratio = 1.6-3.2).
Sodium Carbonate	Anhydrous sodium carbonate with a particle size between 200 and 900 micrometres.
Zeolite A	Hydrated Sodium Aluminosilicate of formula Na12(A1O2SiO2)12 27H2O having a primary particle size in the range from 0.1 to 10 micrometers (Weight expressed on an anhydrous basis).
Enzymes	Protease, Amylase, Lipase, Cellulase
soil release polymer	Soil Release Agents

These formulations are examples of buffering agents useful for spraying-on the granular detergent materials herein

	A	B
C12LAS	3.15	3.15
C12-C18FAS	4.0	4.0
STPP	28.0	28.0
Sodium Carbonate	14.0	14.0
Sodium Sulfate	23.43	18.5
Zeolite A	0.5	0.5
Miscellaneous	2.4	2.4
Moisture	4.3	4.3
Sodium Silicate (45% active)	1.07	3.2
10% Sodium Bicabonate buffering solution	1.4	4.2
Perfume	0.65	0.65
brightner/FWA 49	0.1	0.1
brightner/FWA 3	0.1	0.1
Enzymes	0.45	0.45
polymers	1.1	1.1
Chelate	0.3	0.3
soil release polymer	0.6	0.6
total	100.0	100.0

The above described compositions are suitably made as follows:

(1) STPP, sodium sulfate, sodium carbonate and recycle fine product are mixed at high shear mixer such as CB mixer.

(2) The powdered mixture is mixed with C12-C18 FAS (paste is 70% active) paste and a polymer in the mixer to make agglomerate.

(3) The agglomerate is sprayed C12LAS acid and mixture of sodium silicate and sodium bicarbonate for further agglomeration in another high shear mixer such as Schugi mixer.

(4) The agglomerate is sprayed and coated by mixture of sodium silicate and sodium bicarbonate in a fluid bed dryer and by heated air containing about 0.2% to about 5.0% of carbon dioxide at about 115°C.

(5) The dried agglomerate temperature at outlet of the fluid bed dryer is about 40°C to about 80°C.

(6) The dried agglomerate is cooled by fluid bed cooler at about 10°C to about 20°C dry air.

(7) The agglomerate temperature is about 25°C to about 40°C.

(8) Perfume is sprayed on a the agglomeration in a drum mixer. Other ingredients (Enzymes, bleach, soil release polymers, brighteners) may be added as dry materials.

The embodiments disclosed and represented by the previous examples have many advantages.

It is understood that the foregoing detailed description of examples and embodiments of the present invention are given merely by way of illustration, and that numerous modifications and variations may become apparent to those skilled in the art without departing from the spirit and scope of the invention; and such apparent modifications and variations are to be included in the scope of the appended claims.

WHAT IS CLAIMED IS:

1. A process for making a granular detergent composition comprising the steps of:
(a) granulating a detersive material comprising a detergent surfactant and a builder;
(b) spraying a buffering agent on the granules to substantially coat the granules;
(c) drying the granules with a gas comprising from about 0.05% to 10% by weight of carbon dioxide, wherein the buffering agent has a buffering capability that maintains the pH on the surface of the granule to less than about 13.5.

2. A process according to Claim 1, wherein the buffering agent is selected from the group consisting of sodium and potassium salts of carbonate, bicarbonate, sulfate, hydrogen sulfate, phosphate, monohydrogen phosphate, dihydrogen phosphate, citrate, monohydrogen citrate, dihydrogen citrate, acetate, silicate, pyrophosphate, monohydrogen pyrophosphate, dihydrogen pyrophosphate, , trihydrogen pyrophosphate, tripolyphosphate, monohydrogen tripolyphosphate, dihydrogen tripolyphosphate, trihydrogen tripolyphosphate and mixtures thereof.

3. A process according to Claim 3, wherein the buffering agent is present from about 0.5% to about 50% by weight of the composition.

4. A process according to Claim 1, wherein the detergent surfactant comprises from about 5% to 80% of the composition and is selected from the group consisting of anionic surfactants, nonionic surfactants, zwitterionic surfactants, ampholytic surfactants, cationic surfactants, and mixtures thereof.

5. A process according to Claim 1, wherein the gas comprises from about 0.2% to about 5% by weight of carbon dioxide.

6. A granular detergent composition made according to the process of either of claims 1 or 5.

7. The granule detergent composition according to Claim 6, wherein the granule has a delta E difference of less than 2.0 and an Odor evaluation of at least 7.0.

8. The granular detergent composition according to Claim 7, wherein the granule has a delta E difference of less than 1.0 and an Odor evaluation of at least 8.0.

9. The granular detergent composition according to Claim 7, wherein the granular detergent composition is packed in a package having less than 50 g/m2/24 hours of moisture vapour transmission rate (MVTR).

10 The granular detergent composition according to Claim 9, wherein the package material is selected from the group consisting of polyethylene, polypropylene, polyethylene terephthalate (PET), laminate coated paper and mixtures thereof.

INTERNATIONAL SEARCH REPORT

Inter onal Application No
PCT/US 99/28317

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D11/00 C11D17/06 C11D7/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	column 1, line 50 -column 2, line 4; claim 12; examples	6

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X	column 2, line 40 -column 3, line 27; claims	6

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X	claim 1; example 1	6

A	EP 0 643 129 A (PROCTER & GAMBLE) 15 March 1995 (1995-03-15)	1-4
X	claims	6

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 July 2000	02/08/2000

Name and mailing address of the ISA	Authorized officer
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1

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INTERNATIONAL SEARCH REPORT

Inte onal Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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